Experimental analysis of a degraded open-cathode PEM fuel cell stack

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Abstract

The well-known challenges to be overcome in PEM fuel cell research are their relatively low durability and high costs for the platinum catalysts. Thus, this work focuses on factors that impact durability and the links to the fuel cell performance. Therefore a degraded, open-cathode, 20-cell, PEM fuel cell stack, which was used in a laboratory test station for characterization experiments, was analyzed experimentally. Voltage transients during external perturbations, such as changing temperature, humidity and stoichiometries show that degradation affects individual cells quite differently throughout the lifetime of the stack. Electrochemical impedance spectroscopy (EIS) data presents non-reversible catalyst layer and membrane degradation of several cells. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) are in progress in order to validate the results of the electrical analysis and elucidate catalyst and membrane degradation.

Keywords: *PEM fuel cell, operating conditions, degradation, EIS*

1 Introduction

PEM fuel cells suffer from several degradation mechanisms that lead to a decrease in lifetime. Degradation of the components is one of the most important fuel cell related research topics at the moment. Although degradation is unavoidable, strategies have to be developed in order to minimize the degradation rates and to improve fuel cell durability. The causes for degradation are based on material properties and defects, assembly issues, operating conditions and maintenance procedures [1].

In this context, electrical and physical-chemical analysis of an already degraded stack can improve the comprehension of the related physical phenomena and lead to the development of control strategies in order to increase the cell's durability. The objective of this work is the investigation, identification and separation of degradation phenomena that occur in the different parts of the membrane-electrode-assembly (MEA) of a PEM fuel cell.

The system under study is the commercially available 100 W, 20-cell PEM fuel cell stack H-100 from Horizon Fuel Cells Technologies. This open-cathode system with an active area of 22.5 cm^2 is self- humidified and air-cooled. It includes a cooling fan directly attached to the fuel cell housing, which removes heat from the stack by forced convection and at the same time provides oxygen to the cathode. The stack was tested under the laboratory conditions shown in Table 1 within 1 year (February 2010 – March 2011). Experiments that have been conducted include EIS, Current Interrupt, Polarization Curves, as well as anode and cathode humidification (0-100% RH) variations and diffusion tests with nitrogen. The test station featured large anode inlet and outlet volumes that were not purged with nitrogen after shut-down.

The stack was operated during this period for approximately 280 h and underwent about 60 start-up/shut-down cycles. A notable voltage decay in cell 1 and 2 was observed, especially against the end of the testing period, which is presented in Figure 1 at different currents.

Table 1. Laboratory operating conditions during lifetime

Parameter	Units	Values
Current	A	0-6
Temperature	ºC	10-60
Reactant humidity	%	0-100

From April 2011 to December 2012 the stack was installed in a demonstration plant and was run for about 20 h without data acquisition. Severe degradation was detected since the constant 60 W power demand of the demonstration plant could not be reached anymore. Hence, degradation characterisation experiments were performed, which will be explained in section 2, before taking the stack apart for physical-chemical analysis. The comparison the individual cell voltages at the beginning and end of life is shown in Figure 2. The

voltages of cell 1 and 2 dropped to zero when applying a current higher than 2.5 A.

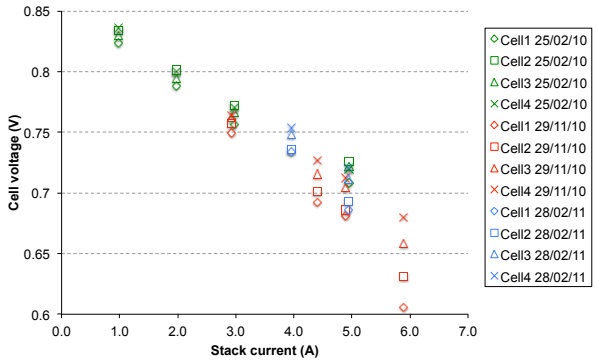


Fig. 1. Voltages of cell 1 to 4 at different current densities and lifetimes

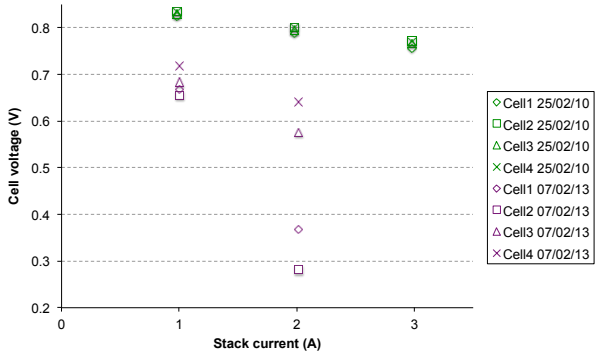


Fig. 2. Voltages of cell 1 to 4 at beginning and end of life

In summary, Figure 1 and 2 show that laboratory operation led to a significant degradation of the first two cells. However, the continued operation at dry ambient conditions in the demonstration plant combined with the months without running the stack resulted in a disabled state for cell 1 and 2. This work tries to elucidate the reasons for the severe degradation of several cells within the stack by electrical and physical-chemical analysis.

2 Experimental analysis of cell voltages

The dynamic voltage responses of degraded cells in the stack, intstalled in an environmental chamber, were studied under different operating conditions and perturbations. LabVIEW data acquisition software was used in conjunction with the National Instruments Analog Input Module for Fuel Cells NI-9206 to measure the stack and single cell voltages. The stack current was measured with a Chauvin Arnoux E3N current clamp. Vaisala HMM211 humidity sensors measured the anode and cathode inlet and outlet dew point temperatures.

2.1 Effect of cathode humidity

Figure 3 shows the changes in the voltages of the first three cells while changing the ambient conditions from 20ºC / 23% RH to 25ºC / 73% RH (represented by the cathode inlet dew point temperature) via an environmental chamber. Once the current increases from 1 to 2 A, cell voltage 2 almost drops down to 0 V. However, during humidification the cell slightly recovers and finally voltage spikes appear which result from oxygen injections into the environmental chamber in order to maintain a homogeneous ambient oxygen concentration. The oxygen concentration oscillates continuously in saw tooth shape about +/-0.05% around a set point of 20.8%. The voltage peaks represent activation of catalyst sites due to higher water content in the cathode catalyst layer, as described in [2], since these spikes cannot be observed at dry conditions. This phenomenon is only present in cell 2, which indicates the advanced catalyst degradation of this cell.

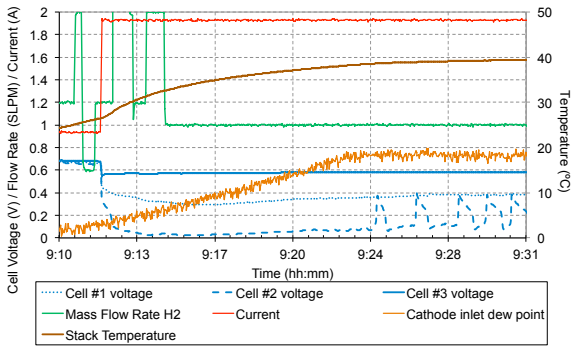


Fig. 3. Degraded cell voltages, current, stack temperature, H_2 flow rate and cathode inlet dew point temperature during humidifying the ambient air from 23 to 73% relative humidity.

2.2 Effect of oxygen concentration

The effect of increasing oxygen concentration in the ambient air was tested manually after a voltage peak. Figure 4 shows how an increase of the oxygen set point of 21.3% manages to stabilize the voltage of cell 2. As explained in section 2.1, part of the active area of cell 2 is degraded. The cathode catalyst layer may have suffered from carbon corrosion during start-up/shut-down cycles, related to the large anode inlet and outlet volumes, as explained in section 2., as well during long operation at open-circuit-voltage (OCV). This may lead to a loss of the carbon support structure and agglomeration of the Pt particles [3]. However, by improving the reaction at non-degraded active sites through humidification and an increased cathode stoichiometry, the cell voltage may partly be recovered, as shown in Figure 4.

The stack cooling by forced convection is coupled to the cathode air supply, as explained in section 1. Thus, even at minimum fan flow rate and

an O_2 concentration of 20.8%, a cathode stoichiometry of around 20 is still guaranteed.

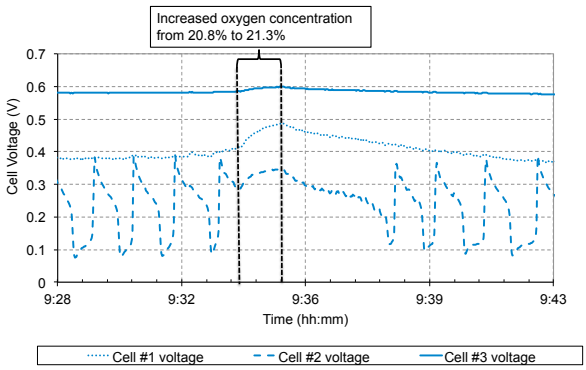


Fig. 4. Degraded cell voltages during a change in the ambient oxygen concentration set point of the environmental chamber controller from 20.8% to 21.3%.

2.3 Effect of anode flow rate

In order to detect degradation of the anode catalyst layer, the anode inlet mass flow rate was increased during the explained unstable voltage transients of cell 2. The result of this change in anode stoichiometry is shown in Figure 5. Doubling the stoichiometry leads to a stabilization of the voltage of cell 2 at around 0.35 V. Obviously increasing the anode stoichiometry affects the cell performance as shown by the voltage of cell 3, for instance, however the performance improvement is nowhere close to the voltage gain of the degraded cell 2. Comparing this test to the changes in H_2 flow rate at dry conditions, as depicted in Figure 3, supports the hypothesis explained in section 2.1, that a significant voltage recovery is only possible under improved stack humidification.

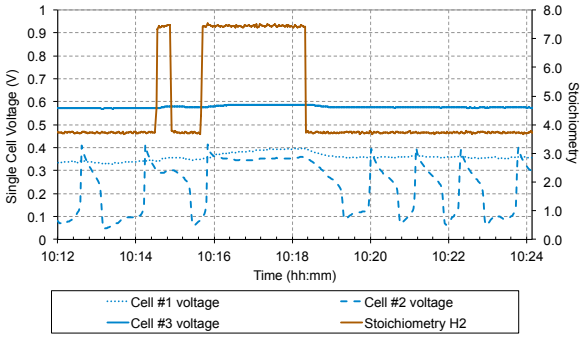
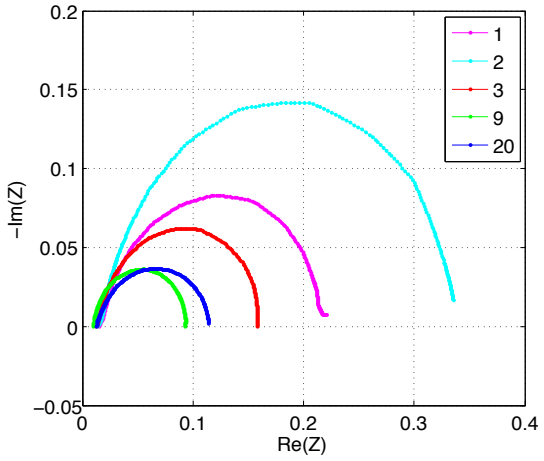


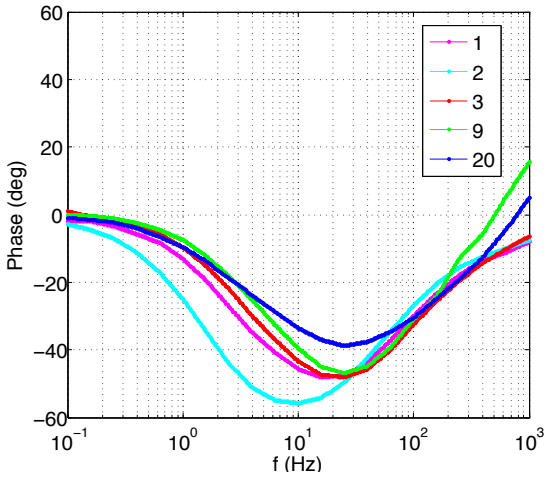
Fig. 5. Degraded cell voltages during a change in the anode stoichiometry.

3 Experimental analysis of impedance data

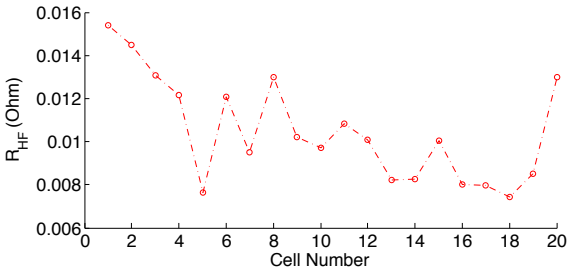
In order to separate the performance losses into membrane and kinetic related losses, EIS of the individual cells within the degraded stack were carried out. EIS are performed using the Agilent 35670A Dynamic Signal Analyzer in conjunction with the electronic load TDI RBL488.



(a)



(b)



(c)

Fig. 6. (a) Nyquist plot, (b) Bode phase diagram and (c) High-frequency resistance of selected cells at a current density of 1 A and 25ºC / 73% RH ambient conditions.

Figure 6(a) shows the Nyquist plot of the impedance data of the three degraded cells (1 to 3) compared to a normally-working cell (9) and the last cell (20), at a current density of 1 A and ambient conditions of 25ºC / 73% RH. As depicted in section 2, cell 2 shows the highest impedance, followed by cell 1 and 3. The difference between

low frequency resistance (R_{LF}) and high frequency resistance (R_{HF}) of cell 2, which gives information about the reaction kinetics of the electrochemical interface [4], increased more than 3 times during lifetime, compared to a normally-working cell. This indicates a reduction in the number of available active sites in the catalyst layer. That this is not a reversible degradation, due to a possible lack of humidification in the catalyst layer, is shown by the change in the phase diagram of cell 2 in Figure 6(b), which indicates a change in the dielectric properties of the double layer capacity [2].

Degradation of the membrane is represented by an increase in the membrane resistance, which is approximately equivalent to the cell's R_{HF}. Figure 6(c) shows that cell 1 and 2 feature elevated membrane resistances compared to the rest of the cells.

4 Discussion and work in progress

All other cells of the stack that are not represented in Figure 6 show similar impedance data as cell 9. Together with the experimental data presented in section 1, this would lead to the assumption that the degradation of the stack started at cell 1, and has proceeded to cell 3, so far. However, also cell 20 shows similar degradation effects in the Nyquist and Bode diagrams, as well as an elevated membrane resistance. Thus, a hypothesis to be proved is that degradation in the stack under study is more severe at cells close to the endplates.

The conclusions and hypothesis of the electrical analysis in the presented work will be evaluated by a physical and chemical examination of degraded and non-degraded cells. In order to perform this analysis, the stack will be taken apart. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) are in progress to elucidate the degradation of the catalyst layers and to find the reason for the more or less distinctive degradation effects on different cells.

5 Conclusions

An experimental study has been performed on a degraded, 20-cell, open-cathode PEM fuel cell stack. Single cell voltage data shows that degradation affected mostly cells located next to the endplates of the stack. However, the most degraded cell is cell 2, which exhibits the highest impedance and the lowest voltage. EIS analysis indicates non-reversible catalyst layer degradation. Observation of voltage transients during changes of cathode humidification as well as anode and cathode stoichiometries shows a distinctive sensitivity of the degraded cells, which indicates a reduction of available active sites. Moreover, EIS data depicts an increased membrane resistance of cell 1 and 2, compared to the rest of the stack, which is a result of membrane degradation. Physical and chemical analysis of different cells within the stack is under way to validate the results from the electrical analysis. The identification of the different degradation mechanisms in this work provides important knowledge in order to improve operating conditions and to design proper system controllers that take into account fuel cell durability.

6 Acknowledgements

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7 References

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